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Colored Dissolved Organic Matter in Sediments and Seagrass Beds and its Impact on Benthic Optical Properties of Shallow Water Marine Environments - Data Analysis and Synthesis, and Student Support

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LONG-TERM GOALS

The optical properties of shallow water coastal environments are a complex function of physical and biogeochemical processes occurring both in sediments and in the water column. Developing models of the optical properties of these environments requires further knowledge of the processes affecting light alteration and modification by biogeochemical reactions in the surficial sediments and at the sediment-water interface. The goal of our work has been to examine one aspect of this problem, namely the impact of dissolved organic matter (DOM) in sediment pore waters on benthic optical properties.

OBJECTIVES

For the past seven years we have been involved in studies of colored dissolved organic matter (CDOM) in sediment pore waters as a part of this award and the previous 5 year CoBOP DRI. We have examined the processes affecting the production of CDOM in sediment pore waters, the mechanism(s) by which this material is transported out of the sediments, and the impact of pore water CDOM on the optical properties of the shallow water benthos (i.e., the sediments, the sediment-water interface and the waters overlying the sediment).

In this project, our objectives are: to analyze, synthesize and write-up our CoBOP data; to continue to collaborate in similar efforts with other CoBOP researchers, in order to maximize our ability to use our combined CoBOP data sets in the examination of the problems outlined above. In the specific context of our work carried out during CoBOP, such efforts would greatly improve our ability to use these results to further understand the influence of the benthos on the optical properties of shallow water environments. In the larger context of the overall goals of the CoBOP project, these activities are important for improving the reliability of the interpretation of hyperspectral remote sensing reflectance data in optically shallow coastal waters.

APPROACH

Our approach involves the continued analysis of CoBOP data collected by my lab, as well several collaborative efforts involving other CoBOP PI's. Our work is carried out by myself (as PI of the project), Mr. Scott Kline (a Ph.D student working with me on this project who plans to use his work

here as a the major part of his Ph.D. dissertation), Mr. Xinping Hu (a Ph.D student working with me on this project who plans to use his work here as a portion of his Ph.D. dissertation).

WORK COMPLETED

In the past year we submitted one manuscript for publication (to *Marine Chemistry*) on CoBOP-related work, and presented one poster at the 2003 ASLO Aquatic Sciences Meeting. We published a manuscript in *Limnology and Oceanography* based on ancillary data collected during CoBOP project.

Although not yet in finished form, work was carried out this year on Scott Kline's Ph.D. dissertation (which will result in at least two additional manuscripts for publication).

RESULTS

The results in the past year are best summarized by the abstracts for the manuscripts and talks discussed above.

1. Fluorescent Dissolved Organic Matter in Marine Sediment Pore Waters (David J. Burdige, Scott W. Kline and Wenhao Chen; manuscript submitted to *Marine Chemistry*)

Fluorescent dissolved organic matter (FDOM) in sediment pore waters from contrasting sites in the Chesapeake Bay and along the mid-Atlantic shelf/slope break was studied using 3-dimensional fluorescence spectroscopy. Benthic fluxes of FDOM were also examined at the Chesapeake Bay sites. The major fluorescence peaks observed in these pore waters corresponded to those observed in the water column. These included peaks ascribed to the fluorescence of humic-like material (peaks A, C and M), as well as protein-like peaks that appear to result from the fluorescence of the aromatic amino acids tryptophan and tyrosine. In these pore waters we also observed a fourth humic-like fluorescence peak (A'). These four humic-like peaks appeared to occur in two distinct fluorescence emission bands (peaks A and M in one band and peaks A' and C in another band), in a manner that was analogous to that observed for more simple chromophores. The emission band containing peaks A' and C was red shifted relative to the peak A and M emission band.

Humic-like fluorescence increased with sediment depth at almost all stations, and was closely correlated with total DOC. This fluorescence appeared to be a tracer for the refractory, relatively low molecular weight pore water DOM that accumulates with depth during sediment diagenesis. Fluorescence-DOC relationships indicated that larger relative amounts of humic-like FDOM were seen in anoxic sediments versus sub-oxic or mixed redox sediments. By extension, these observations suggest that refractory humic-like compounds (in general) are preferentially preserved in sediment pore waters under anoxic conditions. The sources of these humic-like fluorophores are not well understood although a simple model is presented here which proposes that different types of organic matter (e.g., marine vs. terrestrial) as well as internal transformations of DOM or FDOM may lead to the occurrence of these humic-like fluorophores. This model is consistent with a wide range of data on FDOM in marine as well as freshwater systems. Protein-like fluorescence showed no coherent depth trends in sediment pore waters, other than the fact that pore water fluorescence intensities were greater than bottom water values. Based on the results of benthic flux studies in Chesapeake Bay sediments, it

appeared that protein-like fluorescence was associated with high molecular weight DOM intermediates of organic matter diagenesis (e.g., dissolved peptides and proteins) produced near the sediment-water interface. In contrast, this did not appear to be the case in sediment pore waters. Benthic flux studies at the Chesapeake Bay sites further indicated that sediments represent a source of chromophoric DOM to coastal waters, although further work will be needed to quantify their significance in terms of other known sources of this material (e.g., riverine input, phytoplankton degradation products).

2. Fluorescence of Pore Water Dissolved Organic Matter in Shallow Water Marine Carbonate Sediments as a Function of Seagrass Density (S W. Kline and D.J. Burdige; manuscript and dissertation in prep.)

Pore waters from shallow water carbonate sediments in the Bahamas were collected over a period of three years on a seasonal basis (winter and early summer) to examine the factors controlling sediment organic matter remineralization. Sediments at these sites range from bare oolitic sands to sediments underlying dense seagrass meadows (*Thalassia testudinum*). In this study, pore water samples were analyzed for their fluorescence properties using EEMS (excitation - emission matrix spectroscopy) focusing on humic-like and protein-like peaks observed in such fluorescence spectra. Dissolved organic matter (DOM) fluorescence in shallow water carbonate pore waters showed an overall increase with depth over the upper 20 cm of sediment. This is similar to that seen in siliciclastic estuarine and shelf/slope break sediments. However, in the interval from the sediment-water interface to approximately 2 cm depth, only minor depth changes were observed in the shallow water carbonate pore waters relative to gradients deeper in the sediment. This may indicate the possible occurrence of advective mixing of pore waters and bottom waters in these surface sediments. DOM fluorescence was observed to be a function of seagrass density at these sites. Sites with high seagrass density showed the largest fluorescence values, while sites with no seagrass (oolitic sands) showed the smallest fluorescence values. Furthermore, dense seagrass sites showed seasonal trends in DOM fluorescence, with winter samples having lower fluorescence values than summer samples. The fluorescence/DOC ratio was also lower in shallow water carbonate sediments as compared to siliciclastic estuarine and shelf/slope break sediments. Further examination of the data will involve using it in an attempt to differentiate between types of DOM present in the sediment pore waters (terrestrial versus marine) and examine the degradation and remineralization mechanisms affecting both DOM and total organic matter. We will also use the data to specifically examine the role of seagrasses in the cycling of DOM in these shallow water carbonate sediments.

3. Dissolved Carbohydrates and Organic Matter in Carbonate Sediments, Lee Stocking Island, Bahamas (X. Hu and D.J. Burdige; poster presented at to the 2003 ASLO Aquatic Sciences Meeting).

Total dissolved carbohydrates (DCHO) and total dissolved organic carbon (DOC) were examined in carbonate sediments with different seagrass densities. In dense seagrass sediments, DCHO concentrations generally increased with depth, while DOC profiles showed variable mid-depth maxima (≥ 5 cm). DCHO and DOC levels were also higher in summer than in winter. In sparse and no seagrass sediments, DOC showed little seasonal or depth variations. While DCHO had little seasonal variations, the concentrations reached maxima just below sediment-water interface. DCHO/DOC ratios showed distinct differences with regard to seagrass densities. The ratios reached maximum values at ~15cm, ~5cm and ~2cm for dense, sparse and no seagrass sediments, respectively. All of the differences are

likely related to sediment-seagrass interactions, since differences in seagrass densities lead to differences in both the organic matter input and the diagenetic environment in the sediments. Finally, larger calcium pore water gradients in dense seagrass sediments (indicative of carbonate dissolution) suggested that part of the DOC and DCHO may come from the release of organic matter either strongly adsorbed to, or integrally a part of, the carbonate mineral matrix.

4. Impact of seagrass density on carbonate dissolution in Bahamian sediments (D.J. Burdige and R.C. Zimmerman [MLML; now at ODU]; *Limnology and Oceanography* 47:1751 (2003)).

Carbonate dissolution has been widely observed in shallow water tropical sediments. However, sediment budgets have generally not been closed with respect to the amount of acid required to produce the observed carbonate dissolution. Recently it has been suggested that enhanced oxygen transport into sediments through the roots and rhizomes of seagrasses might play a role in resolving this mass balance problem. We conducted studies of seagrass-carbonate sediment interactions around Lee Stocking Island, Exuma Islands, Bahamas to further examine this problem. Our studies showed that alkalinity, total dissolved inorganic carbon (ΣCO_2) and Ca^{2+} increased with depth in the pore waters, while pH and calculated carbonate ion concentration decreased with depth. These observations are consistent with the occurrence of carbonate dissolution in these sediments. The magnitude of pore water alkalinity, ΣCO_2 and Ca^{2+} changes were also related to seagrass density, with the largest gradients seen in the sediments of dense seagrass beds. Calculations suggested that less than ~50% of the O_2 needed to drive aerobic respiration (and ultimately carbonate dissolution via CO_2 production) could be supplied by transport processes such as diffusion, bioturbation and physical pore water advection. Furthermore, the O_2 needed to balance the carbonate dissolution budget could be provided by the transport of <15% of the photosynthetically derived O_2 to the sediments through seagrass roots and rhizomes without enhancing the removal of carbonate dissolution end-products. Thus seagrasses play an important role in controlling the rates of carbonate dissolution in shallow water tropical marine sediments.

IMPACT/APPLICATIONS

Work carried out during CoBOP and during this year of funding has been useful in terms understanding the controls on DOM cycling in marine sediment pore waters, and in examining the extent to which coastal sediments are sources of CDOM to coastal waters. Understanding these sediment sources of CDOM to the water column and their rates of delivery is clearly important in the development of reliable algorithms for the interpretation of hyperspectral remote sensing reflectance in coastal waters.

TRANSITIONS

Based on numerous discussions, our results appear to be of interest to many of the other CoBOP investigators. This has resulted in several collaborative projects at LSI with other CoBOP-funded researchers. In particular, ancillary data we collected during the CoBOP project in conjunction with Dick Zimmerman allowed us to obtain NSF and NOAA-NURP funding to continue work on sediment-seagrass biogeochemistry in the Bahamas.

RELATED PROJECTS

The efforts are closely related to several other CoBOP projects, including those of M. Allison, R. Wheatcroft, A. Decho, F. Dobbs/L. Drake, R. Zimmerman, P. Reid, C. Mazel and R. Zanfeld/E. Boss.

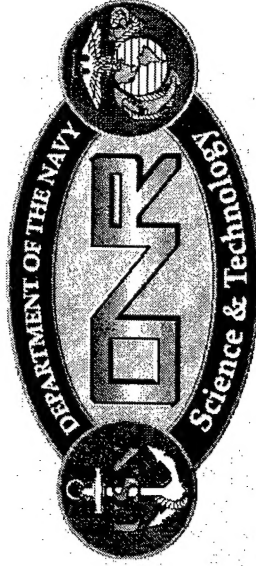
PUBLICATIONS

Burdige D. J. and Zimmerman R. C. (2003) The role of seagrasses in calcium carbonate dissolution in shallow water sub-tropical carbonate sediments. *Limnol. Oceanogr.* in press 47:1751-1763.

Burdige D. J., Kline S. W., and Chen W. (2003) The cycling of fluorescent dissolved organic matter in contrasting marine sediments. ms. in revision for to *Mar. Chem.*

Colored Dissolved Organic Matter in Sediments and Seagrass Beds and its Impact on Benthic Optical Properties of Shallow Water Marine Environments

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Determination of CDOM Sources using Fluorescence Spectroscopy

A Occurrence of Humic-Like Fluorescence Emission Bands

B Similarity of Humic-Like Peaks across Varying
Environments

C Publications and Presentations

- Various talks at national and international meetings
- S Kline's Ph.D. dissertation and ms. in prep. for
Limnol. Oceanogr.
- Burdige, D. J., Chen, W., and Kline, S. A. The cycling of
fluorescent dissolved organic matter in contrasting
marine sediments. ms. in prep. for Mar. Chem.

Pore Water CDOM Fluorescence Peak Ratios (LSI~)

<u>Site</u>	<u>A/M</u>	<u>A'/C</u>
No grass	~ ~ ~ ~ ~	~ ~ ~ ~ ~
Sparse grass	~ ~ ~ ~ ~	~ ~ ~ ~ ~
Dense grass	~ ~ ~ ~ ~	~ ~ ~ ~ ~
Norman's Pond	~ ~ ~ ~ ~	~ ~ ~ ~ ~
Chesapeake Bay & Mid-Atl~shelf/slope break	~ ~ ~ ~ ~	~ ~ ~ ~ ~

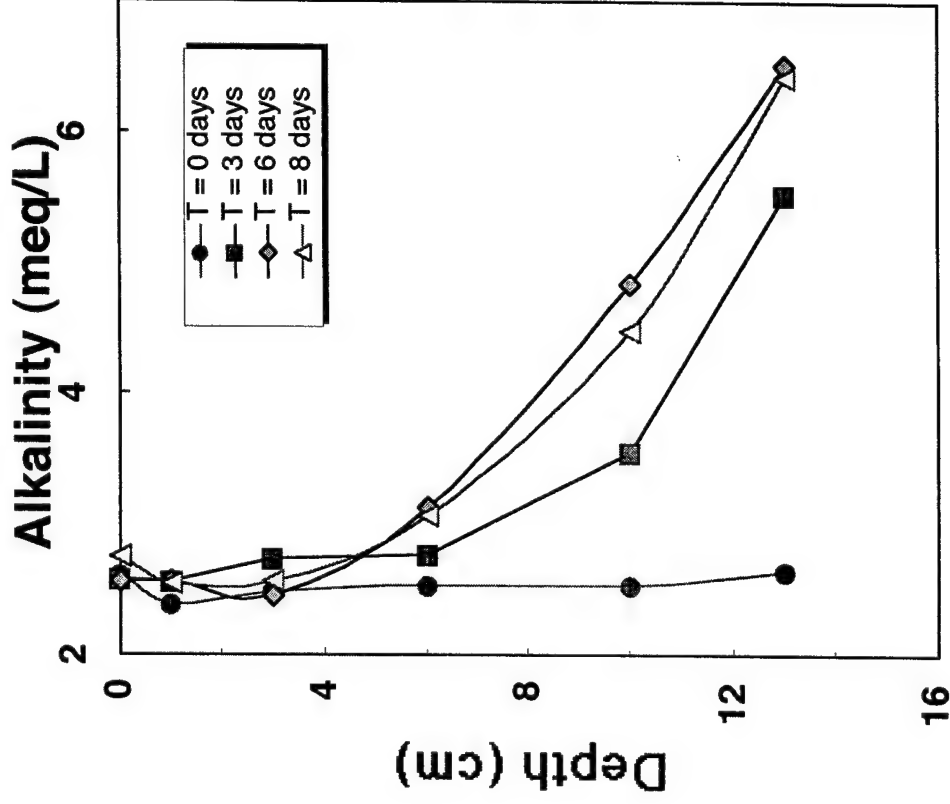
II ~ Determination of CDOM Benthic Fluxes Using Core Incubation Techniques

- A ~ Use whole core incubation techniques – look at the in-growth of chemical parameters
- B ~ Status of work – beginning the modeling of these results to quantify CDOM fluxes from LSI sediments ~
- C ~ Publications and presentations ~ none yet ~ but forthcoming ~

LSI $\sim (\gamma \sim \sim)$ \sim Sparse Grass (BD) site

These and other incubations predict carbonate dissolution rates that range from $\sim \sim \sim \text{mmol m}^{-2} \text{yr}^{-1}$

$\sim \sim$ to $\sim \sim$ time higher than diffusive fluxes



III ~ Inter-calibration of Lab-Based versus *In Situ* CDOM Measurements ~

Here we plan to analyze data collected during side-by-side sediment pore water sampling and CDOM analysis carried out in collaboration with R. Zanfeld and E. Boss (OSU) ~

This involves comparing our techniques for pore water collection and CDOM analyses back in the lab with their use of diver-operated versions of the WET Labs AC ~ and SAFire instruments ~ modified to draw pore waters out of the sediments for *in situ* analysis ~

Status of work – in discussion

IV~Studies of Pore Water CDOM in Monterey Bay Sediments

This effort involves the analysis of pore water CDOM data collected in Monterey Bay sediments in conjunction with Dick Zimmerman's group~

These results will also become part of a larger comparative analysis of our entire pore water CDOM data set collected during CoBOP~

Status of Work – Analyses completed

Publications and Presentations ~S~Kline's Ph.D~
dissertation and associated publications

V~Studies of Carbonate Mineral Fluorescence

(with Mead Allison and Charlie Mazel)

The fluorescence of carbonate minerals has been well known for quite some time although the origins of this fluorescence are not well understood~

EEMS spectra suggest that the source of this fluorescence is organic matter trapped in (or intimately associated with) the carbonate mineral matrix~

In addition to using these results to further examine the origin(s) of the fluorescence signal in carbonate minerals we will also examine the possible contribution of this sediment fluorescence signal to the upwelling light field~

Status of work ~Analyses complete~beginning discussions about a manuscript

VI ~ Studies of the Role of Seagrasses as Sources of CDOM to Coastal Waters

This work involves using pore water and water column CDOM measurements made by our group and Emmanuel Boss and Ron Zaneveld to further understand the role of seagrasses as sources of CDOM to shallow coastal waters~

AC ~ time series at the Rainbow Gardens closure site
(~ ~ ~)

Status of work ~ Presented last week at the Ocean Sciences meeting; beginning discussions about a manuscript

VII ~ Other CoBOP ~ Supported Work

Studies of shallow water carbonate dissolution and the role of seagrasses in mediating this process (in conjunction with Dick Zimmerman)

Status of the work ~ one manuscript in revision for Limnol ~ Oceanogr ~ new NSF grant to continue this work (as of ~/~/)

Back to LSI in May '~~ and '~~!!!!

